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(54) Title: METHOD OF COATING OPTICAL FIBRES (57) Abstract A "wet-on-wet" method of coating an optical glass fibre, so as to provide thereon an ultra violet radiation-cured clear primary coating and an ultra violet radiation-cured pigmented secondary coating, comprises: a) applying to the fibre a clear primary curable liquid coating composition, b) applying directly onto the curable primary composition a pigmented curable secondary liquid coating composition, and c) simultaneously curing both the primary and secondary coating compositions using ultra violet radiation, and acylphosphine photoinitiator being used as an initiator during the curing of the primary coating composition.		

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Method of Coating Optical Fibres

The present invention relates to a method for coating an optical glass fibre and to the coated fibre so produced.

5

Optical fibres are widely used in the communications field because of their ability to carry large amounts of information over long distances. They are normally made of silica glass, although polymer clad silica fibres and
10 polymer core fibres are known. In order to protect the fibres from physical damage and also from deterioration due to environmental agencies such as water, it is conventional to apply at least one protective coating to the freshly drawn fibres as an integral part of the production process.
15 Thus a liquid coating composition(s) which on curing will provide the protective coating(s) is applied "in-line", i.e. after the fibre is drawn from the molten preform but before the fibre is taken up onto the winding drum. Materials that cure on exposure to radiation such as
20 ultraviolet light are favoured in the industry due to their rapid cure rate, enabling the coated fibre to be produced at high speed. Curable liquid material containing (usually) photoinitiator is applied to the fibre and curing is effected by (usually) ultraviolet radiation using an
25 appropriate radiation source (e.g. ultraviolet lamps). Liquid formulations comprising ethylenically-terminated urethane oligomers, as typified by urethane - acrylate oligomers, and copolymerisable ethylenically unsaturated

liquid solvents therefor, the latter often being called "reactive diluents" in the art, (both types of material being well known in the optical fibre coating art), are especially favoured due to their low viscosity, rapid cure
5 response and the desired physical properties of the cured coatings. These cure to solid polymeric coatings having desired properties.

Because of the difficulty of achieving all the
10 required properties in a single coating, an optical fibre is frequently provided with at least two polymeric coatings. A soft primary buffering coating of low modulus and low glass transition temperature (T_g) is applied nearest to (usually directly contacting) the optical fibre,
15 having an ability (inter alia) to cushion the fibre from mechanical stresses and to avoid microblending problems which would lead to attenuation of signal. A harder (higher T_g), higher modulus secondary coating is applied on top of the primary coating to provide (inter alia)
20 toughness, abrasion resistance, and general ease of handling. The primary layer can be cured before the application of the secondary, or after so that both layers are cured at the same time.

25 For ease of identification, e.g. to facilitate the selection of the optical fibre from others in a cable, a coloured coating layer is frequently used. The coloured coating may be applied as a tertiary ink layer (coated over

the secondary coating) or the secondary coating may itself be coloured. Where a tertiary ink layer is used this may be either a UV-cured pigmented resin or a solvent borne ink containing a polymer and pigment. Coloured secondary
5 coatings are normally made by the inclusion of a particulate pigment material in the secondary coating composition. The use of coloured (pigmented) secondary coatings eliminates the need for a separate, off-line inking process and allows coloured fibre to be produced
10 directly on a draw tower. The primary coating is normally unpigmented, and is usually clear.

As mentioned above, there are two main methods used in the production of such dual coated fibres. In the "wet-on-
15 dry" method, the primary liquid coating composition is applied from a die to the fibre and then cured by (usually) ultraviolet (uv) radiation (e.g. from uv lamps); the secondary liquid coating composition is then applied to the cured primary coating and then itself cured by a second uv
20 radiation source. In the alternative "wet-on-wet" process, the secondary liquid coating composition is applied over the uncured liquid primary coating composition, and then both are cured simultaneously using the same uv radiation source (e.g. a single set of uv lamps). These alternative
25 methods are also referred to generally in EP-A-0539030, directed towards providing urethane oligomers for improving the properties, notably lower water absorption, of the coatings.

This invention is concerned with the "wet-on-wet" method of coating which has obvious advantages from the point of view of increased coated fibre production rate and more economic use of radiation equipment (one set of uv
5 lamps instead of two).

In EP-A-0539030, laboratory tests are disclosed in which coatings are separately applied to glass and their mechanical properties tested. In Examples recommended for
10 use as a primary coating of an optical fibre the initiator may be Irgacure 651, a benzil ketal type initiator or Lucirin TPO, an acylphosphine oxide type initiator, while in Examples recommended for use as a secondary coating Lucirin TPO is again used. However, there are no examples
15 which illustrate either a "wet-on-dry" or a "wet-on-wet" process and problems associated with the performance of a wet-on-wet process, especially when the secondary coating is to contain a pigment, are not addressed. Indeed the possible presence of such a pigment is not mentioned.

20

However, problems do indeed arise with this wet-on-wet process, namely that the primary coating composition must be cured through the secondary composition, and this is particularly significant if a pigmented secondary coating
25 is used. The pigment will absorb and scatter some of the uv light, reducing the amount available for the photoinitiator. This is particularly true of the shorter wavelengths and so pigmented coatings themselves usually

contain initiators in which the absorbtion spectrum extends to longer wavelengths, typically up to 450nms, to overcome this scattering problem. (If the photoinitiator absorbs at even longer wavelengths it will of course be coloured, and 5 give rise to undesirable yellowing on cure). One class of photoinitiator which is well known to be suitable for curing pigmented coatings is the acylphosphine oxide group of photoinitiators.

10 Thus, WO-A-90/13579 for example discloses (inter alia) the use of these photoinitiators in pigmented secondary optical fibre coatings.

Nevertheless, the inclusion of an acylphosphine oxide 15 in the secondary coating still leaves a problem of inefficient (slow) or incomplete cure in the primary coating composition in a wet-on-wet coating method, in view of the reduction in light intensity reaching the primary layer due to absorption and scattering by the pigment 20 particles and due to the absorbtion by the photoinitiator in the secondary coating - i.e. still significantly reducing the amount of uv radiation available for the primary photoinitiator.

25 We have now found that, surprisingly, the use of an acylphosphine oxide (APO) as a photoinitiator in the primary coating composition provides a significant advantage in the wet-on-wet process. The reduction in cure

speed, or degree of cure as a function of uv exposure, caused by the pigmented secondary is much improved in comparison to when other primary photoinitiators are used.

- 5 Thus according to the present invention there is provided a method for coating an optical glass fibre so as to provide thereon an ultra violet radiation-cured clear primary coating and an ultra violet radiation-cured pigmented secondary coating, which method comprises:
- 10 a) applying to the fibre a clear primary curable liquid coating composition,
- b) applying directly onto the curable primary composition a pigmented curable secondary liquid coating composition, and
- c) simultaneously curing both the primary and secondary
- 15 coating compositions using ultra violet radiation, characterised in that the primary coating composition comprises as an initiator an acylphosphine photoinitiator.

There is further provided according to the invention a

20 coated optical glass fibre which has been made using a method as defined above.

The effectiveness of the APO in this invention method is possibly due to it being less sensitive to the reduction

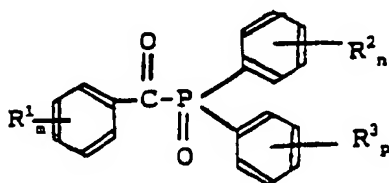
25 in uv intensity caused by the pigmented secondary, or perhaps because its longer wavelength absorbtion enables it to capture light specifically in the region not absorbed or scattered by the pigment - even after the light has passed

right through the secondary coating composition. However, we are not certain of why it is so effective in primary coatings and do not wish to be bound by any theory.

- 5 It is not, in fact, necessary to employ an APO as a initiator in the secondary pigmented coating composition and other, more conventional, photoinitiators known to be effective for secondary pigmented coatings may alternatively be employed. Examples include:
- 10 1-hydroxycyclohexyl-1-phenyl ketone (Irgacure 184), benzil dimethylketal (Irgacure 651), 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one (Irgacure 907), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, all available from Ciba-Geigy AG and 2-
- 15 hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173), available from EM Industries Company.

The acylphosphine oxide photoinitiators used in the primary coating composition preferably fall within those

20 represented by the following formula:



(I)

25

where each of R^1 , R^2 and R^3 is independently an optional C_{1-10} hydrocarbyl group and each of m , n and p is independently 0

to 3. Each of R^1 , R^2 and R^3 is, independently, preferably alkyl or aryl (especially phenyl), and more preferably C_{1-4} alkyl (particularly methyl).

5 Particularly preferred are the 2,4,6-trimethyl benzoyl compounds, and especially 2,4,6-trimethyl benzoyl diphenyl phosphine oxide. This is available from BASF under the trade name Lucirin.

10 The APO may be used as the sole initiator or with at least one other photoinitiator. Preferably the amount of APO is at least 0.5 wt% based on the total weight of photoinitiator used. The amount of photoinitiator used in the primary coating composition (i.e. APO plus other
15 initiator(s) if used) is preferably 2 to 6 wt%, based on the total weight of the composition.

Other types of initiator which may optionally be used with the APO in the primary composition include the
20 following:

1-hydroxycyclohexyl-1-phenyl ketone (Irgacure 184),
2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173),
benzil dimethylketal (Irgacure 651) and benzophenone.

25 The photoinitiators of both primary and secondary compositions may optionally be used together with accelerator compounds (such as amines, for example, methyldiethanolamine) to further enhance photocure rate.

The coating compositions of both the primary and secondary layers will normally (as mentioned above) include at least one ethylenically-terminated urethane oligomer, such as a urethane-acrylate oligomer, and at least one
5 reactive diluent, which on curing will provide a solid polymeric coating. Examples of these components both for primary and secondary coatings are given in EP-A-0539030 and WO-A-90/13579. The types of urethane-acrylate and reactive diluent in the compositions will be selected
10 bearing in mind the required properties of the primary and secondary layers (as discussed above). This is well known in the art.

The compositions of the primary and secondary coating
15 compositions may also if appropriate include other components, such as stabilizers, antioxidants, slip agents, wetting agents, adhesion promoters and flatting agents. Again, this is well known in the art.

20 The primary coating compositions are liquid and normally have a viscosity (at ambient temperature (25°C)) within the range 20 to 120 poise, measured using a Brookfield viscometer, Spindle 31 at 1½ revs/min. The cured primary coating will usually have thickness within
25 the range 10 to 40 µm.

The pigmented secondary coating composition will usually contain an amount of pigment which is within the

range of from 0.1 to 5 wt% based on the total weight of the composition, although the range may vary according to the pigment type.

- 5 The average particle size will usually be within the range 0.5 to 2 μm , often $\leq 1\mu\text{m}$, although contrary to the teaching of WO-A-91/13579 we do not find it necessary to grind the pigment so as to ensure there is no detectable amount of particles of size $> 1\mu\text{m}$.

10

White pigments which may be used include TiO_2 .

Coloured pigments include azo and phthalocyanine compounds and carbon black.

15

The thickness of the cured secondary coating will usually be within the range 10 to 40 μm . Its viscosity (25°C) will usually be within the range 20 to 120 poise.

- 20 As discussed, cure of the coating compositions in the invention method is effected by uv radiation, which for the purposes of this invention includes visible light near the uv region. Usually, the uv range used will be from 200 to 450 nm.

25

Each radiation-curable liquid coating composition may be applied to the optical fibre by conventional methods. Usually the fibre (already coated with liquid primary

composition when applying the secondary coating) or a bundle of such fibres, is drawn through a bath containing the coating composition. The rate is usually within the range 3 to 15 ms⁻¹. The emerging fibre, having both liquid
5 primary and secondary compositions thereon, is then subjected to uv radiation to effect simultaneous curing to the solid primary and secondary coatings.

Embodiments of the invention will now be described in
10 more detail with reference to the following Examples and accompanying drawings, in which:

Fig. 1 shows differential photocalorimetry (dpc) graphs of heat flow vs. time for curing of a primary coating containing 4 wt% Irgacure 184 (outside the
15 invention), (a) without a secondary coating, (b) with a clear secondary coating and (c) with a blue secondary coating, the secondary coatings also containing 4 wt% Irgacure 184;

Fig. 2 shows dsc graph of heat flow vs. time for
20 curing of a primary coating containing 3 wt% Lucirin TPO (within the invention), (a) without a secondary coating and (b) with a blue secondary coating containing 4 wt% Irgacure 184;

Fig. 3 shows graphs, obtained by dpc, of % conversion
25 for curing of a primary coating containing 4 wt% Irgacure 184 (outside the invention), (a) without a secondary coating and (b) simultaneously through an uncured blue secondary coating;

Fig. 4 shows graphs, obtained by dpc, of % conversion for curing of a primary coating containing 3 wt% Lucirin TPO (within the invention) (a) without a secondary coating and (b) simultaneously through an uncured blue secondary coating;

Fig. 5 shows a schematic assembly of a slide containing a liquid resin for a secondary coating for use in dpc analysis; and

Fig. 6 shows a schematic view of a dpc apparatus for determining the effect of simultaneously curing superimposed primary and secondary layers.

Examples 1-5

1) Preparation of Coating Compositions A and B for Primary Layer

Each of coating compositions A and B for primary layers contained a polyester urethane-acrylate oligomer, a mixture of two monofunctional acrylate monomers, a trifunctional acrylate monomer, an alkoxysilane methacrylate monomer and a photoinitiator. In composition A, the initiator was 3 wt% Lucirin TPO, an APO photoinitiator commercially available from BASF, namely 2,4,6-trimethyl benzoyl diphenyl phosphine oxide, while in composition B the photoinitiator was 4 wt% Irgacure 184, a photoinitiator commercially available from Ciba-Geigy AG, namely 1-hydroxycyclohexenyl-1-phenyl ketone (a 4 wt% of Irgacure 184 was chosen so as to provide a reasonable rate of cure for the material cured alone, i.e. not through a

secondary coating; see below).

2) Preparation of Coating Compositions for Secondary Layer

5 A clear first composition containing a mixture of two urethane acrylate oligomers, a monofunctional acrylate monomer and a trifunctional acrylate monomer was made up for use as a first, clear secondary layer and a second composition was made up, which was identical to the first
10 composition but additionally contained 0.29 wt% of a blue pigment, for use as a second, blue secondary layer.

3) Differential Photocalorimetric (dpc) Analysis

 The effect of the presence of a curing, coloured
15 secondary coating on the rate of curing of a primary coating was determined by dpc analysis, conducted as explained below with reference to Figs. 5 and 6.

 As shown in Fig. 5, a slide assembly, generally
20 indicated as 10, was made up by firstly cutting out a hollow rectangular spacer 4 from a polyethylene film having a thickness of approximately 25 μm (actually measured at $23.4 \pm 0.9 \mu\text{m}$). This was placed over a quartz microscope slide 2, and a coating resin composition for a secondary
25 layer was coated over the microscope slide 2 in the hollow part 5 of spacer 4. A film 6 of polyethylene also of approximately 25 μm thickness was then placed over the resin, followed by a second quartz microscope slide 8. The

slide assembly was then clamped together to expel excess resin and leave a liquid resin film of approximately 25 μm thickness.

5 Referring now to Fig. 6, a dpc apparatus consists of a unit generally indicated as 12 similar to that of a conventional differential scanning calorimeter (dsc) containing a dsc head 14 on which were placed an open dpc aluminium pan 16 having a base coated internally with a
10 coating resin composition for a primary coating and an empty reference pan 18. The unit 14 was covered with a quartz window 20 on which the slide assembly 10 containing the resin composition for the secondary coating was located. UV light was then directed towards the dpc
15 apparatus in the direction of arrows 22, 24, so that light reaching the dsc pan 16 and empty reference pan 18 had to pass firstly through the resin composition for the secondary layer.

20 This apparatus therefore provided simultaneous curing of the resin compositions for both primary and secondary layers, and therefore provided a model for assessment of the probable behaviour of the resin compositions in a practical wet on wet process used in the preparation of
25 optical fibres containing both primary and secondary layers. In particular, since the sample containing the resin composition for the secondary layer was remote from the dsc pan containing the resin composition for the

primary layer, the cure exotherm of the composition for the secondary layer was not detected by the dpc and so did not interfere with the determination of the cure rate by dpc of the composition for the primary layer.

5

For each coating composition for a primary coating, traces were obtained for each of

(a) a quartz slide/polyethylene film assembly with no secondary coating resin composition present;

10 (b) the assembly of (a) but with the presence of a clear (unpigmented) secondary coating resin composition; and

(c) the assembly of (a) with the presence of a secondary coating resin composition containing 0.29 wt% of
15 a blue pigment.

The traces are shown in Figs. 1-4, and results derived therefrom set out in the Table below.

20 The traces were obtained during curing in a nitrogen atmosphere for 10 minutes of samples of approximately 1 mg in weight, using a DuPont dpc apparatus (DPC VI.OE DuPont 9900).

16

Table

	Example	1	2	3	4	5
	Primary Resin	A	A	B	B	B
5	Photoinitiator in Primary	TPO	TPO	Irgacure 184	Irgacure 184	Irgacure 184
	Wt% photoinitiator in primary	3	3	4	4	4
	Secondary Resin	None	Blue	None	Clear	Blue
10						
	DPC Parameters for Primary Coating					
	Enthalpy (J/g)	185	184	172	175	168
	Peak Height (W/g)	21.5	17.4	11.1	10.9	5.7
15	Time to peak max (s)	4.2	4.8	6.8	7.6	10.2
	Reacted at peak (%)	24	22.6	22.7	23.8	17.9
	Time(s) to various % conversion:					
20	1%	1.5	1.7	2.2	2.5	3.6
	50%	6.7	8.2	11.7	12.5	3.6
	75%	11.1	14.7	23	23.4	61.1
	90%	19.9	33.1	53.5	53.3	139.6

25

The attached graphs of Figs. 1-4 present the data in two forms. In Figs. 1 and 2 the raw data, as produced directly by the dpc, is shown. No analysis of the data has been carried out here. Figs. 3 and 4 show the percentage conversion versus time plots. These are derived by selecting an end point from the graphs such as Figs. 1 and 2. A computer then calculates the time required to reach certain percentage conversions, based on full conversion at the selected end point. This analysis also produces the data shown in the Table (such as time to peak heat flow, % reacted at peak etc).

From Fig. 1 it can be seen that for primary resin B (outside the invention), containing 4% Irgacure 184, a large reduction in cure rate occurs when the blue liquid resin is placed in the path of the uv beam. This can be seen from a large reduction in peak height (11.1 to 5.7 W/g), and large increases in the times taken to reach various % conversions (see Table). Fig. 1 also shows that when the clear secondary resin is used in place of the blue, very little reduction in cure speed occurs. The effect is therefore due to the blue pigment. The pigment was present only at 0.29 wt%, a low pigment loading. It is likely that even larger effects would be seen with higher pigment levels (e.g. >1%). Fig. 3 shows the effect of the blue pigmented secondary on the percentage conversion graph.

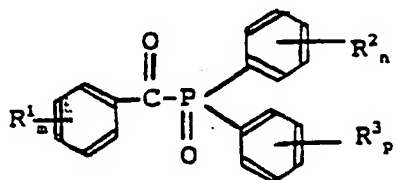
The corresponding plots for primary A (within the invention) containing 3% Lucirin TPO, are shown in Figs. 2 and 4. Fig. 2 shows there is a much less dramatic reduction in cure speed on introducing the blue secondary resin than was found for the primary containing Irgacure 184 (compare Figs. 1 and 2). Similar conclusions result from comparing the percentage conversion graphs (Fig. 4 cf Fig. 3), and from the data in the Table. In particular, introduction of the blue secondary reduces the peak height (maximum rate) by only 19% for primary A compared with 49% for primary B. Similarly, the time to reach 50% conversion is increased by 97% for Primary B, compared with 22% for Primary A.

In short, the above results show that when a film of blue liquid resin composition for a secondary coating is placed between a curing uv source and a resin composition for a primary coating, a smaller reduction in cure speed of the primary coating when the primary coating contains in accordance with the invention, an APO resin, Lucirin TPO as initiator as compared with a primary coating containing Irgacure 184.

Claims

1. A method of coating an optical glass fibre so as to provide thereon an ultra violet radiation - cured clear
 5 primary coating and an ultra violet radiation - cured pigmented secondary coating, which method comprises:
 a) applying to the fibre a clear primary curable liquid coating composition,
 b) applying directly onto the curable primary composition
 10 a pigmented curable secondary liquid coating composition, and
 c) simultaneously curing both the primary and secondary coating compositions using ultra violet radiation, characterized in that the primary coating composition
 15 comprises as an initiator an acylphosphine photoinitiator.
2. A method according to claim 1, wherein the acylphosphine oxide has the formula:

20



(I)

where each of R^1 , R^2 and R^3 is independently an optional C_{1-10}
 25 hydrocarbyl group and each of m , n and p is independently 0 to 3.

3. A method according to claim 2, wherein, in the formula

(I), each of R^1 , R^2 and R^3 is independently selected from C_{1-4} alkyl and phenyl groups.

4. A method according to claim 3, wherein the
5 acylphosphine oxide includes a 2,4,6-trimethyl benzoyl group.

5. A method according to claim 4, wherein the
acylphosphine is 2,4,6-trimethyl benzoyl diphenyl phosphine
10 oxide.

6. A method according to any preceding claim, wherein an
initiator other than the acylphosphine oxide is
additionally optionally present in the primary composition
15 and the amount of acylphosphine oxide present is at least
0.5 wt% based on the total weight of initiator present.

7. A method according to claim 6, wherein an initiator
other than the acylphosphine oxide is present and is
20 selected from 1-hydroxycyclohexyl-1-phenyl ketone,
2-hydroxy-2-methyl-1-phenyl-propan-1-one, benzil
dimethylketal and benzophenone.

8. A method according to any preceding claim, wherein the
25 initiator in the primary composition is present in an
amount of from 2 to 6 wt%, based on the total weight of the
composition.

9. A method according to any preceding claim, wherein the secondary composition has an initiator therein other than an acylphosphine oxide.

5 10. A method according to claim 9, wherein the initiator present in the secondary composition is selected from 1-hydroxycyclohexyl-1-phenyl ketone, benzil dimethylketal, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-
10 1-one and 2-hydroxy-2-methyl-1-phenyl-propan-1-one.

11. A method according to any preceding claim, wherein the pigment in the secondary composition is present in an amount of from 0.1 to 5 wt% based on the total weight of
15 the composition.

12. A method according to claim 11, wherein the pigment has an average particle size of from 0.5 to 2 μm but includes particles of a size greater than 1 μm .

20

13. A method according to any preceding claim, wherein the pigment is selected from TiO_2 , azo and phthalocyanine compounds and carbon black.

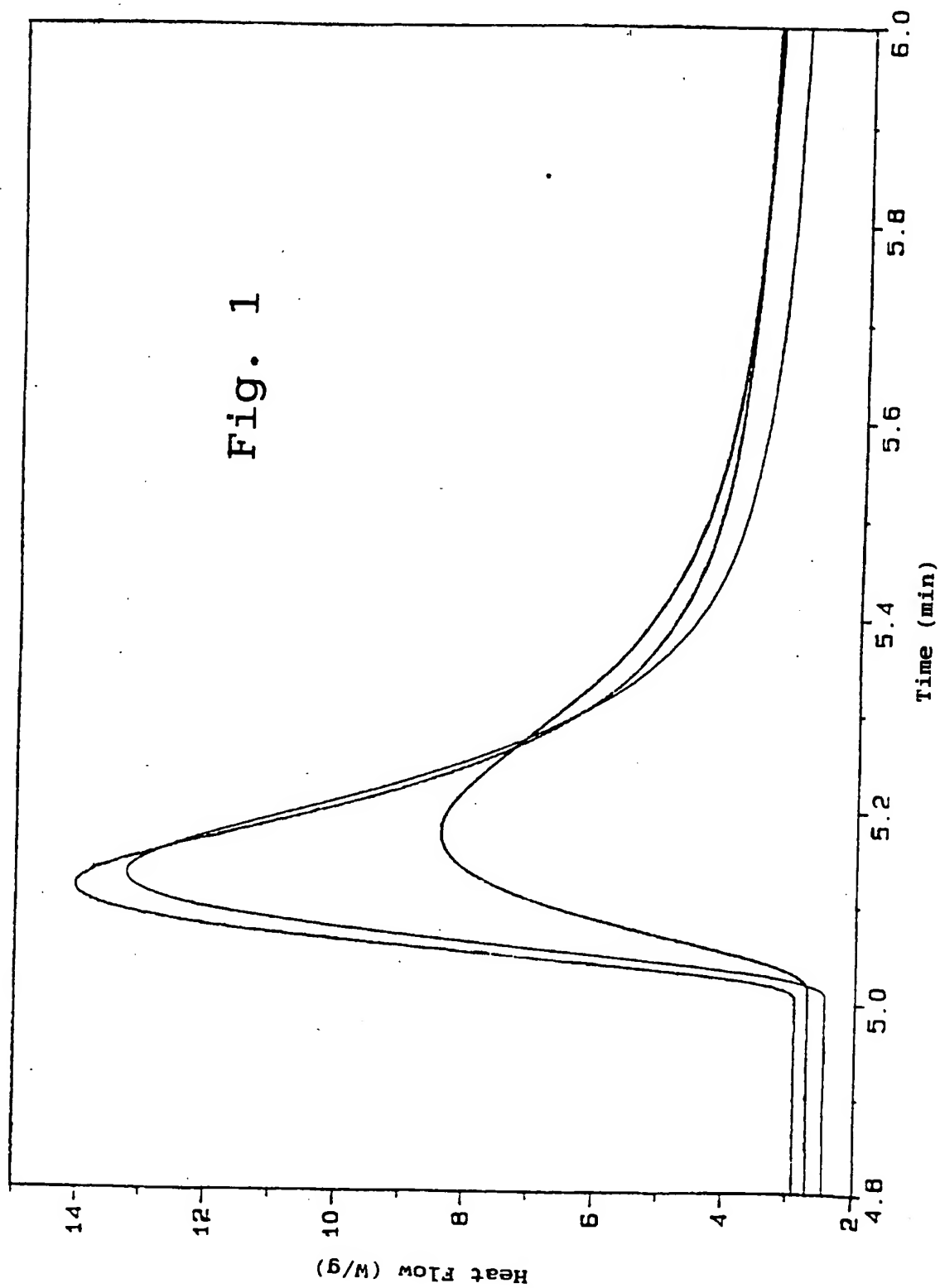
25 14. A coated optical glass fibre which has been made using a method as claimed in claim 1.

15. Use, in a wet-on-wet method of coating an optical

glass fibre so as to provide thereon an ultra violet radiation - cured clear primary coating and an ultra violet radiation - cured pigmented secondary coating, which method comprises:

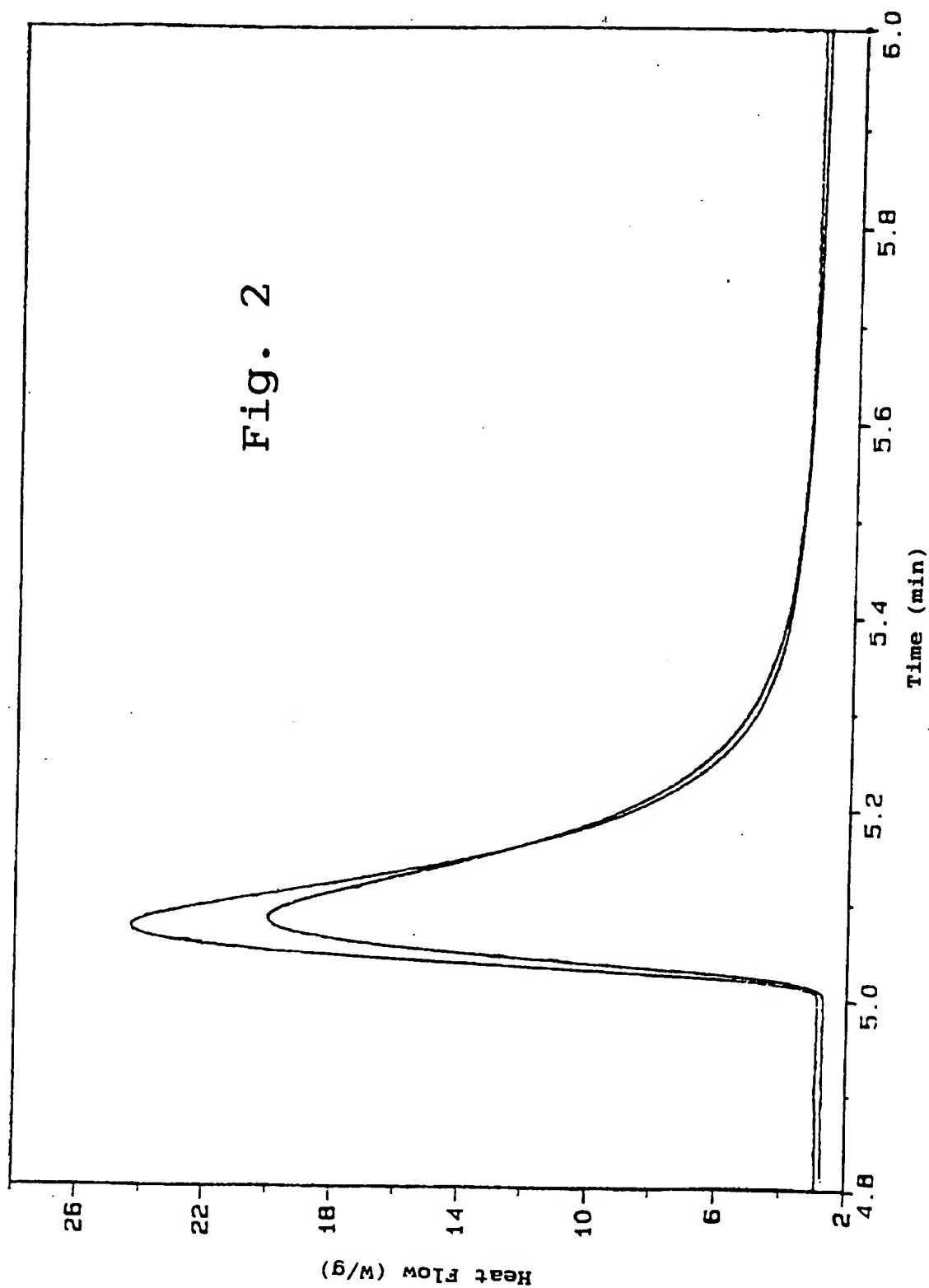
- 5 a) applying to the fibre a clear primary curable liquid coating composition,
- b) applying directly onto the curable primary composition a pigmented curable secondary liquid coating composition, and
- 10 c) simultaneously curing both the primary and secondary coating compositions using ultra violet radiation, of an acylphosphine photoinitiator as an initiator in the primary coating composition.

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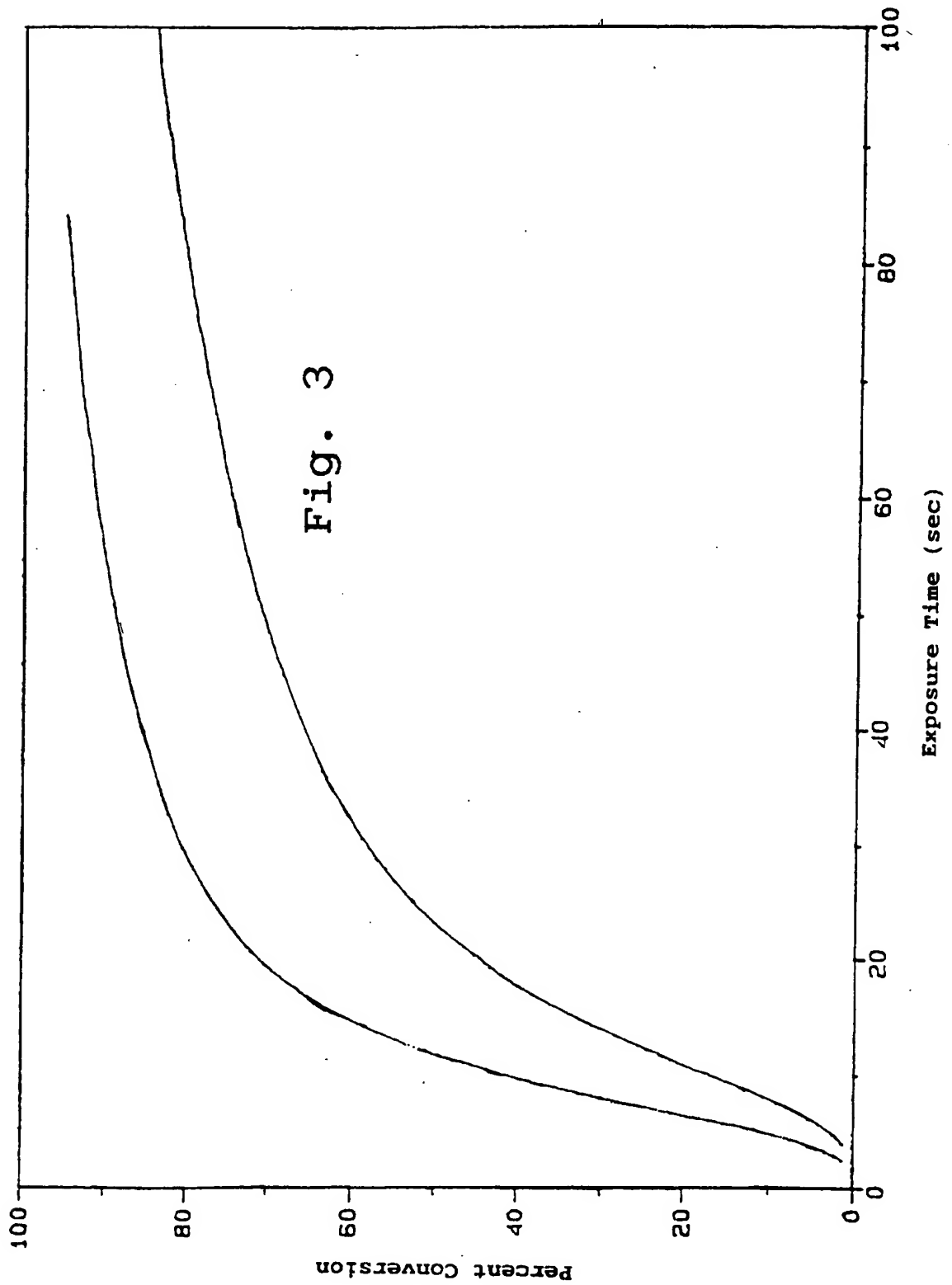
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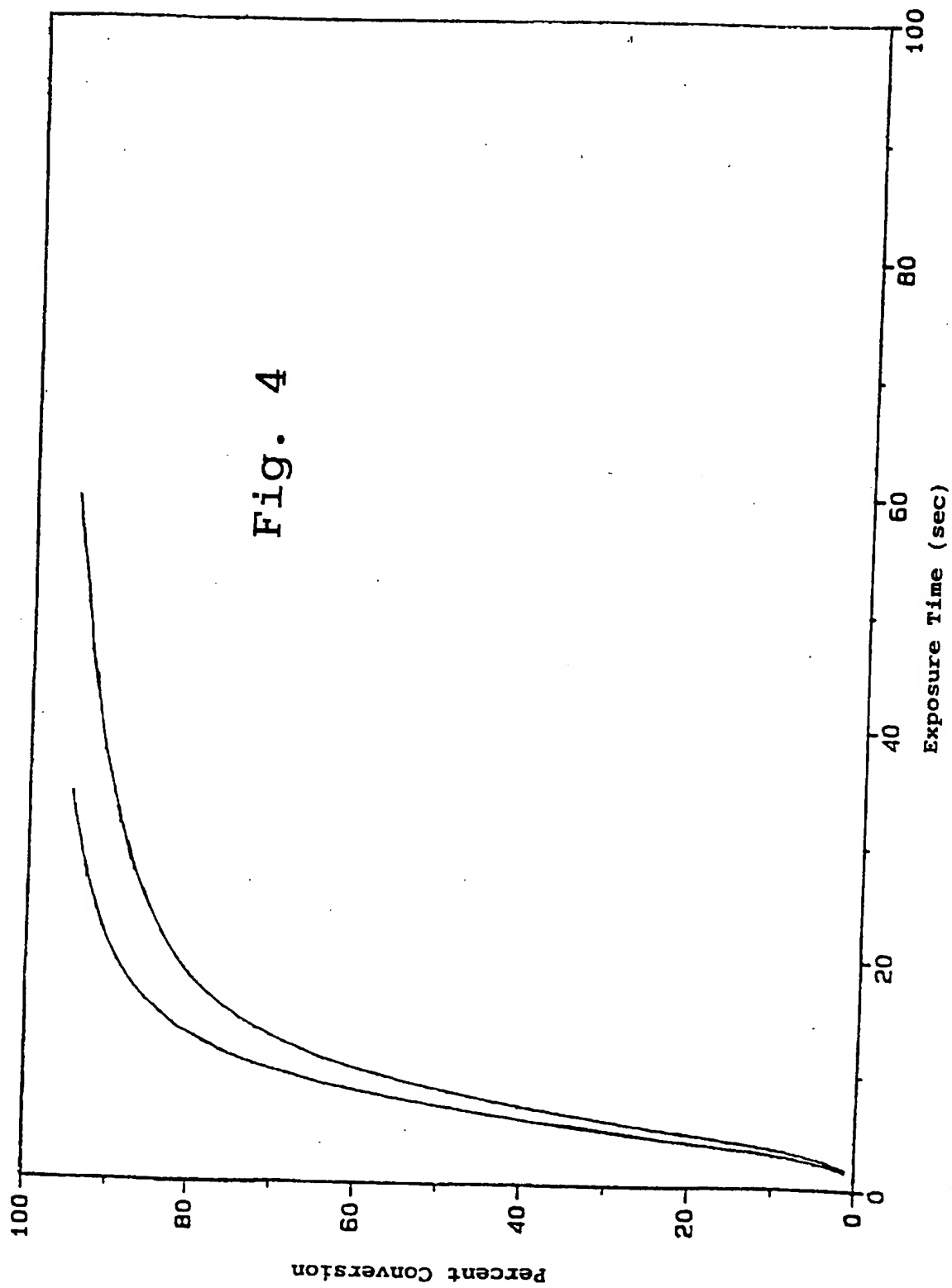
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Fig. 5

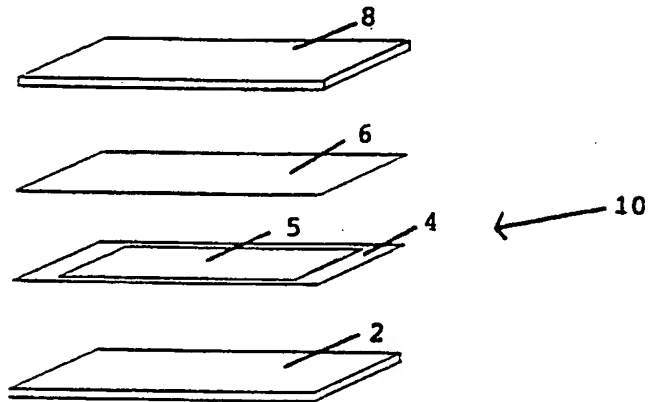
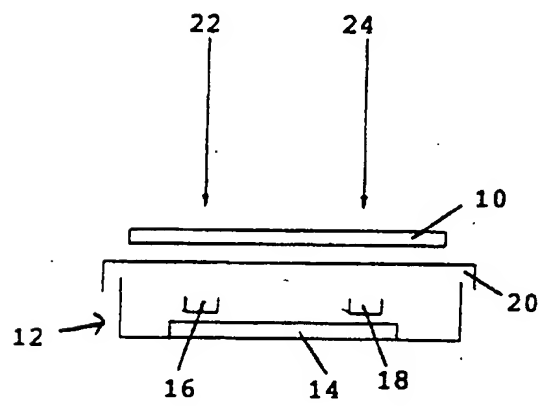


Fig. 6



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/00755

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA,A,2 131 078 (AMERICAN TELEPHONE & TELEGRAPH) 31 March 1995 see page 1, line 9 - page 3, line 29 see page 6, line 29 - page 7, line 7 ---	1-15
Y	WO,A,90 13579 (DESOTO INC) 15 November 1990 cited in the application see page 1, line 9 - page 6, line 4 ---	1-15
A	EP,A,0 539 030 (IMPERIAL CHEMICAL INDUSTRIES PLC) 28 April 1993 cited in the application see page 2, line 1 - line 42 see page 6, line 57 - page 7, line 21 -----	1-15

☐ Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/00755

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